4. Digestions

4.1 Microwave Digestions

4.1.1 Estimation of Weight

Dana Zimmer, Rhena Schumann

Question:

It has to be estimated, which weight of sample material is necessary and in which range the P concentration is in the extract. Th estimation results from estimated P concentrations in environmental samples (see chapter 1) and a standard digestion method.

Known requirements:

- An estimated P concentration range of the sample has to be known (see chapter 1): e.g. in bone char 100…150 g P kg^{-1}. In the following formula it is calculated with 100 g P to make it easier. Calculation for 150 g P are analogue.
- A standard procedure including supposed weigh-in, dilution and so on is selected. Bone char has an organic matrix and can therefore be digested according to a standard method for plant material. Normally, plant material is processed as in the following:
  - Weigh in 0.1 g sample
  - Digest with 5 ml conc. HNO_3 and 3 ml 30 % H_2O_2
  - Fill to 100 ml with ultra-pure water
  - Measure P at ICP-OES
  - The middle standard has a concentration of 10 mg P per litre
  - the P concentration in the extract should be in the range of the middle standard of calibration line and/or not exceed highest standard by a factor of 10

Stepwise procedure to estimate P concentration in the extract according to the standard procedure:

- the estimated P concentration in the sample (100…150 g P per 1000 g) is converted to the standard weigh-in by a ratio equation:

$$\frac{100\ g\ P}{x} \equiv \frac{1000\ g}{0.1\ g}$$

conversion results in the following formula:

$$\frac{100\ g\ P \times 0.1\ g\ weight}{1000\ g} = x = \ 0{,}01\ g\ P$$

In 0.1 g bone char there are 0.01 to 0.015 g P.

- This amount of P in the weigh-in mass corresponds to the P amount in the extract after microwave digestion (from this weigh-in). If after the microwave digestion the extract with HNO_3 and H_2O_2 is filled to 100 ml with ultra-pure water, between 0.01 to 0.015 g P can be expected in the 100 ml extract.

- This P amount in 100 ml extract is converted by the ratio equation to P concentrations per litre:

$$\frac{0.01\ g\ P}{x} \equiv \frac{100\ ml}{1000\ ml}$$

conversion results in the following formula:

$$\frac{0.01\ g\ P \times 1000\ ml}{100\ ml} = x = \ 0.1\ g\ P\ per\ litre$$

- The extract has a P concentration between 0.1 and 0.15 g P per litre. This corresponds to a concentration of 100 to 150 mg P per litre in the extract.

Comparison of the estimated P concentration to the standards:

- Comparison
  - P concentration of the middle standard: 10 mg P per litre
  - P concentration of the extract 100 to 150 mg P per litre

- For a standard weigh-in of 0,1 g bone char and filling to 100 ml the P concentration in the extract is 10 to 15 times as high as the middle standard.

- Conclusion
  - P concentration in the extract should be by a fifth to tenth lower!
- Generally, there are 2 opportunities to achieve this:
  - Decreasing the weigh-in to a tenth: weigh-in only 0.01 g bone char instead of 0.1 g
  - Dilution of extracts by a factor of 5 to 10

Evaluation of pros and cons of both opportunities

Lower weigh-in:

- Advantages
  - Less sample material is necessary.
  - No further dilution of extracts is necessary, which might cause dilution errors.
  - Less extraction agents are necessary.
- Disadvantages
  - If the material can statically charge, lower weigh-in can be problematic.
  - For heterogenic material lower weigh-in can increase standard deviation. Either the material has to be homogenised (e.g. milling) or the number of weight-ins has to be increased.
  - If other elements than P shall be measured, their concentration could fall below the detection limit if the weigh-in decreased.

5- to 10-times dilution

- Advantages
  - No/less problems, which can be caused by lower weigh-in (statically charge, heterogeneity)
  - Other necessary elements are in the measurement range or by different dilution the ideal concentration ranges of different elements can be achieved.
- Disadvantages
  - Dilution error
  - Higher amounts of chemicals are needed.

Decision with weighting of individual points (most important first)

- A lower weigh-in should be considered, if: 1. the material is relatively homogenic, 2. the material is not statically charged during weighing-in, 3. No other elements have to be determined in the extract and 4. less sample material is available.
- A dilution by factor 5 to 10 should be selected, if: 1. other elements have to be determined, 2. the material is heterogenic, 3. static charges could cause problems during weighing-in and 4. sufficient material is available.

Suggestions for adjustment of the digestion method for bone char

The decrease of weigh-in by a factor of ten decreases, at a standard volume of 100 ml, the P concentration in the extract (from 100 to 150 mg l^{-1}) to 10 to 15 mg P per litre and less chemicals are necessary for the extract (Tab. 4.1.1-1). If the volume is filled not to 100 but to 50 ml, the P concentration increased to 20 to 30 mg P per litre. This is still in the measurement range for the ICP-OES, and enables simultaneously to determine other elements. If trace elements such as Cd, Cu and Zn have to be determined, the end-volume can be decreased to 20 to 25 ml. Under theses circumstances the P concentration increased to 40 to 60 mg P per litre. That means that a further dilution of the extracts could be necessary for P measurement.

Table 4.1.1-1 Comparison of methods for extraction of bone char with the original and the adjusted method

method	originally	adjusted
weigh-in	0.1 g	0.01 g
extraction chemicals	5 ml conc. HNO_3 and 3 ml H_2O_2	2.5 ml conc. HNO_3 and 1.5 ml H_2O_2
end volume	100 ml	50 ml
expected P concentration	100 to 150 mg P per litre	20 to 30 mg P per litre

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